NOx storage and reduction over copper-based catalysts. part 3: Simultaneous NOx and soot removal

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ABSTRACT

5% copper catalysts with $Ce_{0.8}M_{0.2}O_\delta$ supports (M = Zr, La, Ce, Pr or Nd) were studied for the simultaneous combustion of soot and removal of NOx by the NSR method. The simultaneous chemisorption of NOx and combustion of soot could be carried out above 375 °C, and nitrates were formed upon NOx chemisorption above this temperature. The nature of the M dopant played an important role in the chemisorption of NOx and in the catalysed soot-NOx reaction. As a general trend, the presence of soot had a negative impact on NOx removal by catalysts with very basic supports but had no effect or a positive influence if the support is not very basic. The combustion of soot has a very negative impact for NOx chemisorption on the catalyst with the most basic dopant ($CuO/Ce_{0.8}La_{0.2}O_\delta$), because the CO_2 formed in the reaction of soot combustion competes with NOx for adsorption sites. On the other hand, soot combustion does not affect NOx chemisorption on the catalyst with the most acidic dopant ($CuO/Ce_{0.8}Zr_{0.2}O_\delta$), and the removal of NOx increases in this case because the reduction of NOx by soot contributes to NOx removal. The simultaneous reduction of NOx to N_2 and soot combustion can be carried out under NSR conditions at 400 °C over the $5\%Cu/Ce_{0.8}Pr_{0.2}O_\delta$ catalyst and with H_2 micropulses, and the NSR process has a positive impact on the catalytic combustion of soot.

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1. Introduction

The main pollutants emitted by Diesel engines are nitrogen oxides and soot [1–6]. In these engines, the air-fuel mixture is compressed and this leads to the reaction between N_2 and O_2 yielding NO. Another pathway to NO formation is the oxidation of nitrogen heteroatoms present in fuel, but the former formation pathway is of greater significance in this type of combustion. As soon as the exhaust gas is released at the exhaust manifold, NO slowly reacts with O_2 forming NO_2, and this $NO + NO_2$ mixture is generically referred to as NOx because the NO/NO_2 ratio depends on the O_2 and NOx partial pressures, total pressure, temperature, contact time and presence of catalysts. The compression of the air-fuel ratio also produces heterogeneities in the composition of the combustion mixture, and the deficit of O_2 in particular spots leads to the partial pyrolysis of some hydrocarbons instead of total oxidation. Once the mixture of gases is released to the exhaust system, the

pressure drops and gas cools, and the partially unburned hydrocarbons condense forming soot nanoparticles. In addition, soot also contains metals coming from lubricant oils and from the engine itself, adsorbed hydrocarbons and sulfur compounds.

There are different strategies for NOx and soot removal from diesel engine exhausts [4–7]. The NSR process (NOx Storage and Reduction) is one of the technologies for NOx abatement, where a storage material is used to chemisorb NOx and a reductant is periodically fed, which, in the presence of a catalyst, reduces the chemisorbed species to N_2. The most widely studied NSR catalyst consists of Pt supported on a barium compound, where barium chemisorbs NOx and Pt accelerates the oxidation of NO to NO_2 and catalyzes the reduction of the chemisorbed NOx species. On the other hand, Diesel Particulate Filters (DPF) are employed to avoid soot release, and the soot collected on the filters must be periodically removed by combustion [1–3]. Catalysts are also used to accelerate soot combustion, and Pt is one of the most active for this purpose.

Combined systems for the simultaneous removal of soot and NOx have also been investigated [8] as this approach would be much simpler than conventional dual-bed configurations

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(deNOx + deSoot). Perovskite [9–13], spinel [14,15], Ce-Zr [16] and Fe-K [17] mixed oxide catalysts have been studied, among others, for the simultaneous removal of NOx and soot. In these studies, NOx were reduced by soot in the presence of a catalyst without the addition of gaseous reductant. However, despite demonstrating that soot-NOx reaction contributed to NOx reduction, the NOx conversion levels were low and additional NOx removal strategies are required. Pisarello et al. [18] also explored this concept and studied the catalytic combustion of soot and the simultaneous reduction of NOx by soot using Co-Ba catalysts with high NOx storage capacity in order to enhance NOx removal. They concluded that the chemisorption of NOx on the catalysts partially inhibits the combustion of soot due to the formation of stable nitrates.

The combination of the NSR technology for NOx removal with the simultaneous combustion of soot over the same NSR catalyst seems to be a more promising option for the abatement of both pollutants in a single catalytic bed, and this technology is usually referred to as DPNR (Diesel Particulate NOx Reduction). Conventional $Pt-Ba/Al_2O_3$ NSR catalysts have been studied for the NOx storage and reduction with H_2 and for the simultaneous combustion of soot, and it has been reported that the NOx storage properties are hindered by the presence of soot [19–21].

In order to lower the cost of the NSR and soot combustion catalysts, noble metal-free formulations are also being investigated, and the goal of the current study is to evaluate the potential employment of noble metal-free copper/ceria-based formulations for the simultaneous removal of NOx and soot. On the one hand, ceria-based oxides are among the most efficient catalysts for accelerating soot combustion [16], and on the other hand, we have recently reported that ceria-supported copper formulations are suitable as NSR catalysts [22,23]. This article is the third of a series devoted to CuO/Ceria NSR catalysts. In the first article $CeO_2 + BaO$ supports were compared [22], and it was concluded that the NSR behaviour of $CuO/(CeO_2 + BaO)$ catalysts with different proportion of CeO_2 and BaO (from 0 to 100% of each component) was similar. In the second article, $CuO/Ce_{0.8}M_{0.2}O_\delta$ (M = Zr, La, Ce, Pr or Nd) catalysts were compared, with the aim of improving the NSR performance of the CuO/CeO_2 catalyst [23]. It was concluded that the acid/basic character of the ceria dopants plays a key role. In the current article, $CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts are studied for simultaneous soot combustion and H_2—NSR deNOx. The study was performed using *operando* DRIFTS in order to understand the reaction pathways and the potential synergies or interferences between the catalytic combustion of soot and the NOx storage and reduction when both processes take place over the same catalyst.

2. Experimental details

2.1. Materials

$CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts with M = Zr, La, Ce, Pr or Nd and 5 wt.% Cu have been used in this study. Details regarding their preparation and characterization were reported elsewhere [23,24].

The model soot used was a carbon black by Evonik-Degussa GmbH (Printex U), with $\sim 100\,m^2/g$, <0.1% of ash, $\sim$5% adsorbed hydrocarbons and with an overall composition, 92.2% C, 0.6% H, 0.2% N and 0.4% S.

Soot + $CuO/Ce_{0.8}M_{0.2}O_\delta$ mixtures were prepared in the so-called *loose contact* mode, which has been suggested to mimic the contact in a DPF filter [25]. The soot-catalyst mixtures were prepared with a spatula in a 1:20 wt ratio. This selected soot:catalyst ratio ensures that the solid bed remains stable during the combustion of soot, which is essential in order to attain spectra throughout the experiment.

2.2. Catalytic experiments

All catalytic tests were carried out under *operando* conditions using a Shimadzu Fourier Transform Infrared Spectrometer (IR Tracer-100) with a Harrick reaction cell coupled to a EcoSys-P mass spectrometer and a chemiluminiscence NOx analyzer (Thermo 42H). The sample holder of the DRIFT was 6.3 mm diameter and 3.3 mm deep with the full volume filled with sample. It should be noted that the infrared spectra obtained represent sample in the top *ca* 0.2 mm layer of the total solid [26].

The reaction cell was designed to allow the reaction gas mixture (50 ml/min; 850 ppm NOx + 5% O_2 + N_2) to pass through the catalyst bed with the gas exit at the bottom. 105 mg of the soot-catalyst mixture were used in the soot combustion experiments, and several reference experiments were also performed with 100 mg of catalysts in the absence of soot.

It is worth mentioning that temperature control and monitoring within the DRIFTS cell is complex and it has been reported that the actual temperature of the catalyst bed can be significantly lower than the set point with reported differences of around 50 °C when the temperature is set at 400 °C [27]. This must be kept in mind during interpretation and in particular, when relating data to information obtained using other devices (e.g reactors).

In all experiments, a background spectrum was recorded as described in each case, which was subsequently subtracted from the spectra recorded under reaction conditions. Therefore, the bands shown in the figures can be assigned to the formation or depletion of species on the catalysts.

Considering previous results [28], it was assumed that CO_2 was the main product of soot combustion and that this can be followed using the *m/z* 44 signal. The formation of CO was ruled out under current soot combustion catalytic experiments because the catalysts studied here are highly selective to CO_2 [28]. In addition, the maximum temperature reached was 500 °C, and CO formation is favoured at higher temperatures.

Temperature programmed experiments were carried out by raising the temperature of the soot-catalyst mixtures until 150 °C in a N_2 flow, and holding this constant for 15 min. A background spectrum was recorded of the catalyst at 150 °C in N_2, and then, the inert gas was replaced by $NOx/O_2/N_2$ and the temperature increased at 10 °C/min until 500 °C. In these experiments, 33 scans were averaged to obtain each spectrum, which were measured in the 4000–1000 cm^{-1} range at 4 cm^{-1} resolution.

Isothermal experiments were performed at 400 °C with soot-$CuO/Ce_{0.8}Pr_{0.2}O_\delta$ mixtures with and without pulses of H_2. In these experiments, the temperature was increased from room temperature to 400 °C under N_2, and then a background spectrum was recorded. The inert gas was then replaced by the $NOx/O_2/N_2$ mixture, and considering this time as 0 min. In the isothermal experiments performed with H_2 pulses (NSR experiments), 100 μl pulses of pure H_2 were fed with frequencies of 30 s starting as soon as the $NOx/O_2/N_2$ gas mixture was delivered to the reaction cell. This frequency is in the range of realistic values proposed by Toyota [29–31].

In the isothermal experiments, the rapid-scan mode was used to follow these experiments with the DRIFT spectrometer, recording one spectrum per second as an average of 7 scans and the Rapid-scan Software (Shimadzu Corporation) used to handle the data. The spectra were obtained with a resolution of 8 cm^{-1} in the 4000–1000 cm^{-1} range. The gas composition was monitored in these experiments with the mass spectrometer, because in the experimental set-up used, the sampling frequency of the mass spectrometer was much faster to that of the chemiluminiscence NOx analyzer and was appropriate for fast screening. Comparison of the NOx concentrations measured by chemiluminiscence and mass spectrometry (*m/z* 30) confirmed that both techniques

provide comparable results. The limitation of following the m/z 30 signal is that it is unable to distinguish NO and NO_2, but rather provides values of total NOx.

3. Results and discussion

3.1. Temperature programmed NOx storage experiments

Fig. 1 shows results of the temperature programmed experiments performed with loose contact soot-catalyst mixtures (except where indicated). The m/z 44 signals corresponding to CO_2 are plotted in Fig. 1a, and these signals can be used to evaluate the combustion of soot. It was confirmed experimentally that in the absence of catalysts, no conversion of soot took place in the range of temperatures of these experiments (150–500 °C). Temperature programmed experiments were also carried out with the catalysts without soot for reference purposes, and the m/z 44 signal monitored with $CuO/Ce_{0.8}Pr_{0.2}O_\delta$ is plotted in Fig. 1a as an example. It was observed that the release of CO_2 due to e.g. carbonate decomposition was negligible with regard to the amount of CO_2 emitted due to soot combustion, and it was therefore concluded that carbonate decomposition does not interfere in the monitoring of soot combustion while following the m/z 44 signal.

The onset temperature for CO_2 release in soot combustion experiments (Fig. 1a) was 375 °C for all catalysts, and most of them showed very similar behaviour. This temperature was consistent with typical literature values for the model carbon black used in this study and for other ceria containing soot combustion catalysts [32,33]. Total combustion of soot was not achieved under these conditions due to a limitation in the maximum temperature attainable in the DRIFTS cell (500 °C). For this reason, the soot combustion capacity of the different catalysts are compared using results obtained in the isothermal experiments, where total soot combustion was achieved.

Figs. 1b and c show the NOx and NO_2 profiles, respectively, monitored using the chemiluminiscence NOx analyzer, during temperature programmed soot combustion experiments. NO is the most abundant of the nitrogen oxides in the gas mixture fed to the reactor, in accordance with typical NOx ratios found for real diesel exhausts. All catalysts accelerated NO oxidation to NO_2 above 300 °C, and the NO_2 percentage increased until approximately 425 °C where the thermodynamic equilibrium was attained (Fig. 1c). The NO oxidation capacities of all catalysts studied were similar, and therefore, any relationship between NO oxidation activity and the different NOx chemisorption behaviour observed in Fig. 1b can be ruled out.

Fig. 1b shows NOx curves as crossing the reference NOx profile obtained using the empty reactor. At low temperatures, the NOx levels obtained with the soot-catalyst mixtures were below the reference level, because NOx was removed from the gas mixture, while above a threshold temperature, all catalysts released NOx and their concentrations were above the reference level. The NOx profiles obtained in reference temperature-programmed experiments performed with the catalysts alone ($Ce_{0.8}Pr_{0.2}O_\delta$ is included in Fig. 1b as an example) were quite similar to those obtained with soot-catalyst mixtures. Therefore, in these experiments, the removal and release of NOx observed with soot-catalyst mixtures can be mainly attributed to NOx chemisorption on the catalysts and to further decomposition of the stored species, respectively. However, the presence of soot had certain effects on the NOx profiles, as will be discussed next.

The nature of the dopant, M, strongly affected the NOx chemisorption-release processes (Fig. 1b). It was concluded from previous temperature programmed experiments carried out using $CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts without soot [23] that the acid/basic

character of the dopants plays a major role in the interaction of NOx with the catalyst support. A correlation was found between the acid/basic character of M and the threshold temperature above which NOx release took place, following the trend:

$$\text{Mostacidic} \Rightarrow Zr^{4+} < \text{none} < Nd^{3+} < Pr^{3+} < La^{3+} \Leftarrow \text{mostbasic.}$$

Some consistencies with this trend are observed in Fig. 1b, but the relationship between acid/basic character of M and the NOx chemisorption/release was not completely fulfilled. For instance, considering the behaviour of the CuO/CeO_2 catalyst (Fig. 1b), Zr^{4+} doping led to a decrease of the NOx chemisorption capacity, which occurred from 150 to 260 °C (Fig. 1b), and also to a decrease of the stability of the chemisorbed NOx species that were released above 340 °C. On the contrary, ceria doping with basic cations such as La^{3+}, Pr^{3+} or Nd^{3+} improved the chemisorption of NOx and enhanced the thermal stability of the stored species with regard to CuO/CeO_2. However, the trends of the NOx storage capacity of catalysts with La^{3+}, Pr^{3+} or Nd^{3+} and of the stability of the stored species deduced from Fig. 1b ($CuO/Ce_{0.8}Pr_{0.2}O_\delta < CuO/Ce_{0.8}La_{0.2}O_\delta \approx CuO/Ce_{0.8}Nd_{0.2}O_\delta$) do not match the trend of basicity of the doping cations ($Nd^{3+} < Pr^{3+} < La^{3+}$). These discrepancies must be attributed to the presence of soot. It is known that carbonaceous materials can react with NOx contributing to NOx reduction [34,35], and it cannot be ruled out that the combustion of soot leads to a localised increase in temperature which enhances the rate of desorption of NOx stored on the catalysts. Also, the chemisorption of CO_2 as a soot combustion product on the catalyst would compete with NOx for storage sites, and it cannot be ruled out that this competition affected the stability of the chemisorbed NOx. The effect of the presence of soot in the NOx removal process is also better studied in the isothermal experiments discussed in the next section.

The nature of the nitrogen species stored on the catalysts during the temperature programmed experiments was monitored by DRIFT spectroscopy. The region 1700–1000 cm^{-1} is shown (Fig. 2) where the most relevant bands due to nitrogen- and carbon-containing species appear. Poly and mono-dentate carbonates usually show bands due to the antisymmetric and symmetric stretching modes of the terminal CO bonds around 1480 and 1350 cm^{-1}, respectively [36]. A certain decrease was observed at these wavenumbers (Fig. 2), because carbonates were progressively replaced by chemisorbed NOx. However, when spectra obtained with soot-catalyst mixtures (Fig. 2) are compared with those obtained in similar experiments performed without soot (Fig. 2 in Ref. [23]), which were previously discussed in detail elsewhere [23], it can be concluded that the extent of depletion of carbonates in experiments without soot was higher than that occurring in the presence of soot. This suggests that part of the CO_2 produced as a soot combustion product becomes chemisorbed on the catalysts.

Before discussing in detail the behaviour of the different species as indicated by bands due to nitrogen species observed in Fig. 2 it is worth mentioning that has been recently reported that the molar absorption coefficients of the overlapping bands of carbonates and nitrates are not identical. For this reason, the true position of the nitrate and nitrite bands cannot be assessed within such complex spectra [37,38]. However, despite this limitation of the system under study, some conclusions can be reached by bearing in mind that the position of the nitrite and nitrate bands indicated in the following discussion may differ from those described for other carbonate-free systems.

Bands attributed to nitrogen-containing species grow with temperature in Fig. 2. A band at 1200–1180 cm^{-1} assigned to bridging nitrites (($M-O)_2 = N$) [39] grew for all catalysts at 150–200 °C, which are probably formed upon NO chemisorption on the catalyst support. At 200 °C a band appeared at 1435 cm^{-1} that can
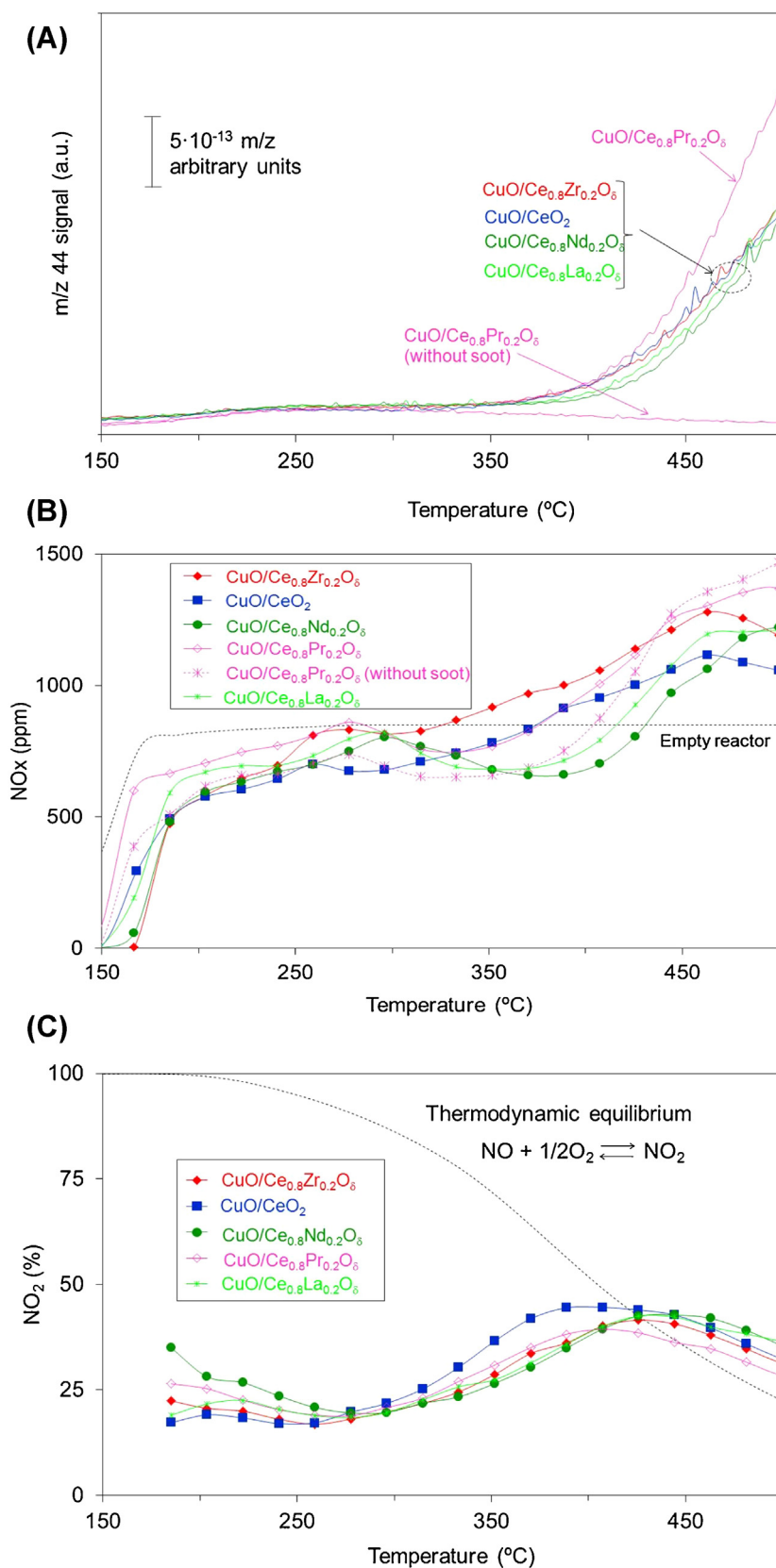
Fig. 1. Temperature programmed experiments performed with 1:20 loose contact soot-catalyst mixtures (otherwise indicated). (a) CO_2 release, (b) NOx concentration and (c) NO_2 percentage with regard to total $NO + NO_2$.
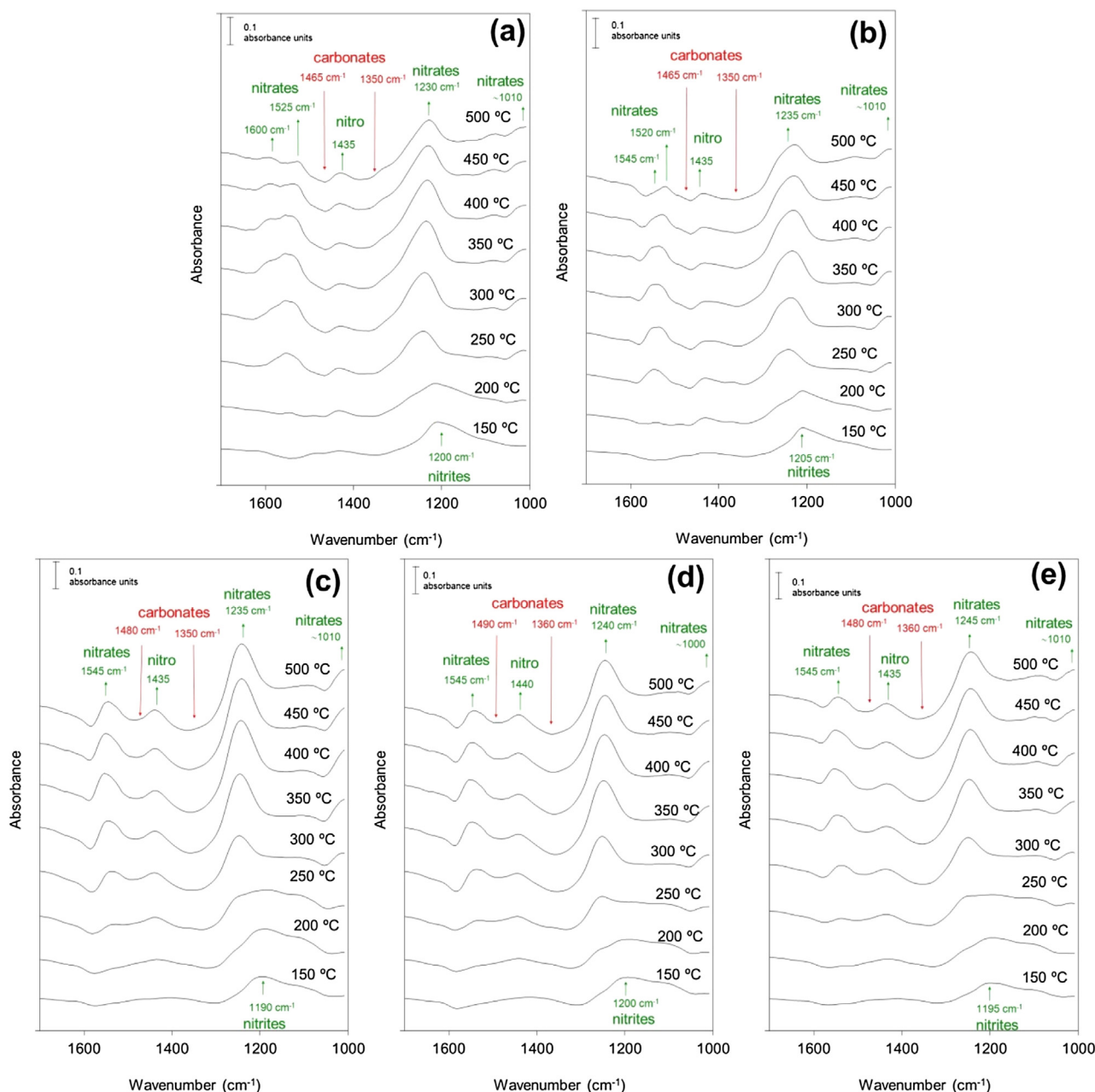
Fig. 2. DRIFT spectra monitored during temperature programmed experiments performed with 1:20 loose contact soot-catalyst mixtures. (a) $CuO/Ce_{0.8}Zr_{0.2}O_\delta$, (b) CuO/CeO_2, (c) $CuO/Ce_{0.8}Nd_{0.2}O_\delta$, (d) $CuO/Ce_{0.8}Pr_{0.2}O_\delta$ and (e) $CuO/Ce_{0.8}La_{0.2}O_\delta$.

be assigned to nitro groups ($M-NO_2$) [39], which remained stable until the maximum temperature of the experiments (500 °C), and nitrate bands were identified in spectra recorded at 250 °C and above. The main nitrate bands appeared around 1545, 1235 and 1010 cm^{-1} and these frequencies are consistent with the presence of monodentate ($M-O-NO_2$) or bidentate ($M-O_2NO$) nitrates [39]. Nitrates can be formed either indirectly by oxidation of nitrogen species already chemisorbed on the catalysts, such as nitrites, or by direct chemisorption of NO_2. Spectra indicate that the nature of the nitrogen species present depends on the oxidation capacity of the catalysts, which increases with temperature following the trend: 150 °C ⇒ nitrites (N (III)) ⇒ nitro (N (IV)) ⇒ nitrates (N (V)) ⇒ 500 °C

In conclusion, these temperature programmed experiments provide evidence that the simultaneous chemisorption of NOx

and combustion of soot can take place above 375 °C with the $CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts. Above this temperature, NOx species were mainly stored in the form of nitrates, indicating that the oxidation capacity of the catalysts was sufficiently high to oxidise N (II) (in NO) to N (V). Also, evidence regarding the consequence of soot combustion on the NOx storage process were observed. The combustion of soot affected the thermal stability of the NOx species chemisorbed on the catalysts, and several hypothesis could be postulated to explain this: the local increase of temperature due to the exothermic combustion of soot destabilises the stored species, soot reacts with the chemisorbed NOx species and/or the CO_2 yielded as a combustion product of soot competes with NOx for chemisorption sites on the catalysts.
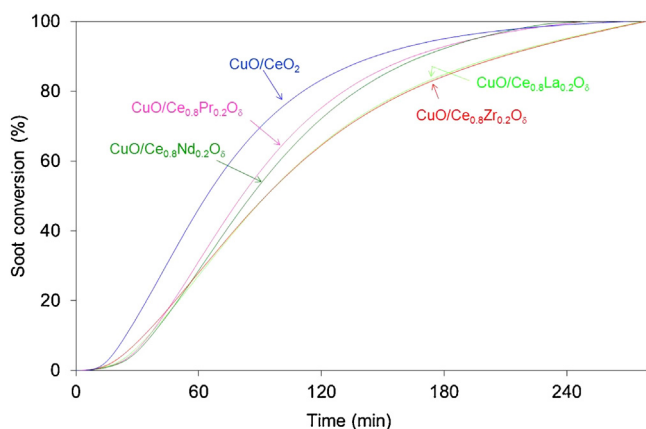
Fig. 3. Soot conversion in isothermal experiments performed at 400 °C with 1:20 loose contact soot-catalyst mixtures (without H_2 pulses). Uncatalysed soot combustion did not take place in these conditions.

3.2. Isothermal experiments at 400 °C without H_2 pulses

Isothermal experiments were carried out at 400 °C with soot-catalyst mixtures. This temperature was selected on the basis of results of the previous temperature programmed experiments, where it was observed that the onset temperature for the catalytic combustion of soot with $CuO/Ce_{0.8}M_{0.2}O_\delta$ was 375 °C. However, the soot combustion rate measured under isothermal conditions at 375 °C was too slow to properly screen catalysts performance, and for this reason it was increased to 400 °C. It is important to note that the uncatalyzed reaction did not take place at a measurable rate at this temperature. It was also previously demonstrated [23] that the elimination of NOx with the $CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts could be achieved at 400 °C using NSR procedures and therefore, this temperature is appropriate to study the simultaneous removal of NOx and soot.

The m/z 44 signal was used to monitor the release of CO_2 for the isothermal experiments carried out at 400 °C with soot-catalyst mixtures, and from this release the conversion of soot was calculated. The isothermal experiments were conducted until total conversion of soot, that is, until the m/z 44 signal reached the baseline level. In all isothermal experiments where total conversion of soot was attained, the mass balance of carbon was properly closed with an error below 5% in all cases, and this indicated that the potential release of CO as a soot combustion product and subsequent accumulation of CO_2 on the catalysts had a marginal contribution to the estimation of soot conversion using the m/z 44 profile.

The soot conversion profiles obtained in experiments performed without H_2 pulses are compiled in Fig. 3. The most active catalyst of those studied was CuO/CeO_2, and all M dopants led to a delay in the soot conversion profiles. This observation is consistent with results reported for different ceria-based soot combustion catalysts [32,40]. It is known that dopants improve the thermal stability of ceria and enhance the mobility of oxygen within the ceria lattice, and these benefits are very relevant for ceria catalysts thermal-threated at high temperatures (roughly above 600–700 °C). However, for ceria catalysts calcined at lower temperatures (500 °C in this study) the presence of dopants have zero or negative effect in mild-temperature soot combustion because they have a diluting effect. That is, there are less cerium cations per unit mass of catalyst and the Ce^{4+}/Ce^{3+} couple responsible for the high soot combustion catalytic activity of these materials is negatively affected.

The removal of NOx during the catalytic combustion of soot at 400 °C was evaluated, and the profiles obtained are included in

Table 1
Amount of NOx removed from the gas stream at 400 °C (in $\mu molNOx/g_{catalyst}$) in experiments without and with soot.

Catalyst	Without soot[a]	With soot[b]	With soot–Without soot
$CuO/Ce_{0.8}Zr_{0.2}O_\delta$	166	320	154
CuO/CeO_2	168	421	253
$CuO/Ce_{0.8}Nd_{0.2}O_\delta$	198	228	30
$CuO/Ce_{0.8}Pr_{0.2}O_\delta$	368	389	21
$CuO/Ce_{0.8}La_{0.2}O_\delta$	366	176	−190

[a] NOx are chemisorbed on the catalyst.
[b] NOx are chemisorbed on the catalyst and reduced by soot.

Fig. 4. The NOx removal profiles obtained in similar experiments performed with only the catalysts (without soot) are also included for comparison. This comparison is useful in order to identify the different NOx removal pathways and the weight of each to the total removal.

All $CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts chemisorbed NOx from the gas stream, as deduced from the NOx removal profiles (Fig. 4) of experiments performed without soot, and the NOx removal levels dropped to zero once the catalyst was saturated. NOx chemisorption on the catalysts also took place in isothermal experiments performed with soot-catalyst mixtures. However, the presence of soot strongly affected this chemisorption in some cases, and the nature of the M dopant played an important role. For instance, the NOx removal profiles obtained with $CuO/Ce_{0.8}Zr_{0.2}O_\delta$ (Fig. 4a) in experiments with and without soot were similar during 25 min, and after this time, the removal of NOx was higher in the experiment performed with soot. This indicated that the soot-NOx reaction contributed to NOx removal. In the case of the $CuO/Ce_{0.8}Zr_{0.2}O_\delta$ catalyst, the NOx-soot reaction only contributed to NOx removal when the catalyst reached a certain level of saturation and continued until total consumption of soot. This suggests that NOx chemisorption occurs preferably to the soot-NOx reaction.

The NOx removal behaviour of the CuO/CeO_2 catalyst (Fig. 4b) was qualitatively similar to that described for $CuO/Ce_{0.8}Zr_{0.2}O_\delta$ (Fig. 4a; note that Zr^{4+} is the most acidic dopant among those studied), but it changed for catalysts doped with basic cations (M = Nd, Pr and La; Fig. 4c–e, respectively). For instance, the removal of NOx by the catalyst with the most basic cation ($CuO/Ce_{0.8}La_{0.2}O_\delta$ Fig. 4e) drops significantly in the presence of soot, and the effect of soot on the removal of NOx over $CuO/Ce_{0.8}Nd_{0.2}O_\delta$ (Fig. 4c) and $CuO/Ce_{0.8}Pr_{0.2}O_\delta$ (Fig. 4d) lies between those described for the catalysts with the most acidic (Zr^{4+}) and most basic (La^{3+}) cations.

The amounts of NOx removed from the gas stream under isothermal conditions at 400 °C in the presence and absence of soot were quantified and compiled (Table 1). As it has been already indicated, the removal of NOx in experiments performed without soot must be only attributed to NOx chemisorption on the catalysts while the reduction of NOx by soot additionally contributed to NOx removal in experiments performed with soot-catalyst mixtures. As previously discussed [23], the amounts of NOx chemisorbed on the catalysts in the absence of soot increased with the basic character of the M dopant. Note that, in Table 1, the basicity increases from top to bottom (most acidic $\Rightarrow Zr^{4+}$ < none < Nd^{3+} < Pr^{3+} < La^{3+} $\Leftarrow$ most basic). On the other hand, the removal of NOx in experiments performed with soot did not follow the trend with respect to M basicity. The greatest removal of NOx was achieved with CuO/CeO_2 (421 $\mu molNOx/g_{catalyst}$), followed by $CuO/Ce_{0.8}Pr_{0.2}O_\delta$ (389 $\mu molNOx/g_{catalyst}$), and the poorest being $CuO/Ce_{0.8}La_{0.2}O_\delta$ (176 $\mu molNOx/g_{catalyst}$).

It is interesting to analyze the differences between the amounts of NOx removed in experiments performed with and without soot, and these values are also included in Table 1. The effect of soot on the removal of NOx was most detrimental for the catalyst with the most basic dopant ($CuO/Ce_{0.8}La_{0.2}O_\delta$; −190 $\mu molNOx/g_{catalyst}$),
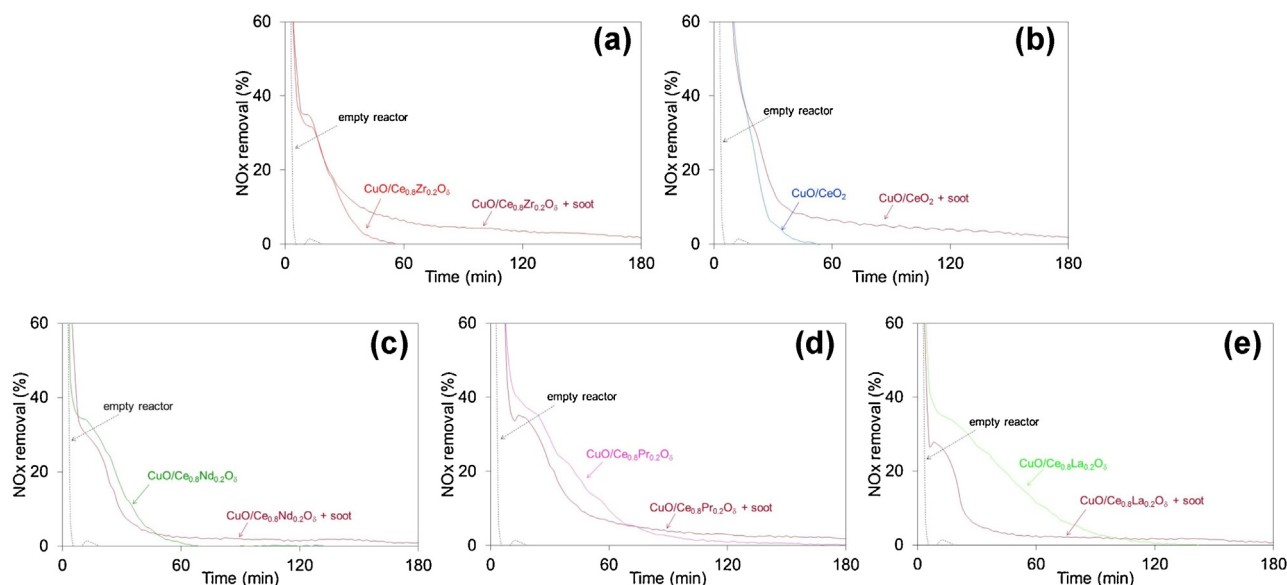
Fig. 4. NOx removal in isothermal experiments performed at 400 °C with CuO/Ce$_{0.8}$M$_{0.2}$O$_\delta$ catalysts and with 1:20 loose contact soot-catalyst mixtures (without H$_2$ pulses). (a) CuO/Ce$_{0.8}$Zr$_{0.2}$O$_\delta$, (b) CuO/CeO$_2$, (c) CuO/Ce$_{0.8}$Nd$_{0.2}$O$_\delta$, (d) CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$ and (e) CuO/Ce$_{0.8}$La$_{0.2}$O$_\delta$.

that is, the presence of soot hinders the chemisorption of NOx on CuO/Ce$_{0.8}$La$_{0.2}$O$_\delta$ and the contribution of the soot-NOx reaction to NOx removal was low, the net balance being clearly negative. The same conclusion was obtained by other authors that also studied the chemisorption of NOx in the presence of soot on catalysts with very basic adsorbents, such as Pt-Ba/Al$_2$O$_3$ [19,20]. On the other hand, for the other two catalysts with basic dopants (CuO/Ce$_{0.8}$Nd$_{0.2}$O$_\delta$ and CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$) the negative effect of soot on the chemisorption of NOx was compensated by the removal of NOx by reduction with soot, and the net balances were close to zero (30 and 21 μmolNOx/g$_{catalyst}$). The presence of soot was clearly positive in terms of NOx removal using catalysts without dopant (CuO/CeO$_2$) or with an acidic dopant (CuO/Ce$_{0.8}$Zr$_{0.2}$O$_\delta$), confirming that the soot-NOx reaction contributed to NOx removal without significantly impacting on the chemisorption of NOx. These results and others [19–21] lead us to believe that the negative effect of

soot on NOx storage is only prevalent for catalysts with very basic character, and therefore, the acid/basic properties of the catalyst must be optimized to avoid the negative effect of soot but also to maximize NOx removal as much as possible. Ceria cation doping seems to be an appropriate approach for this purpose.

Different hypotheses have been proposed to explain the negative effect of soot on NOx storage on Pt-Ba/Al$_2$O$_3$ catalysts. It has been proposed that the combustion of soot ages the catalysts by causing Pt sintering and Ba agglomeration [21]. However this hypothesis is inconsistent with the fact that the negative effect of soot on NOx removal disappears when H$_2$ is fed to reduce the stored NOx species [41]. Some authors have proposed that the negative effect of soot on NOx storage on Pt-Ba/Al$_2$O$_3$ is due to the chemisorption of the CO$_2$ produced as a product of soot combustion product [42] and others suggest that the presence of carbon destabilises the chemisorbed NOx species [19]. In our opinion, these two
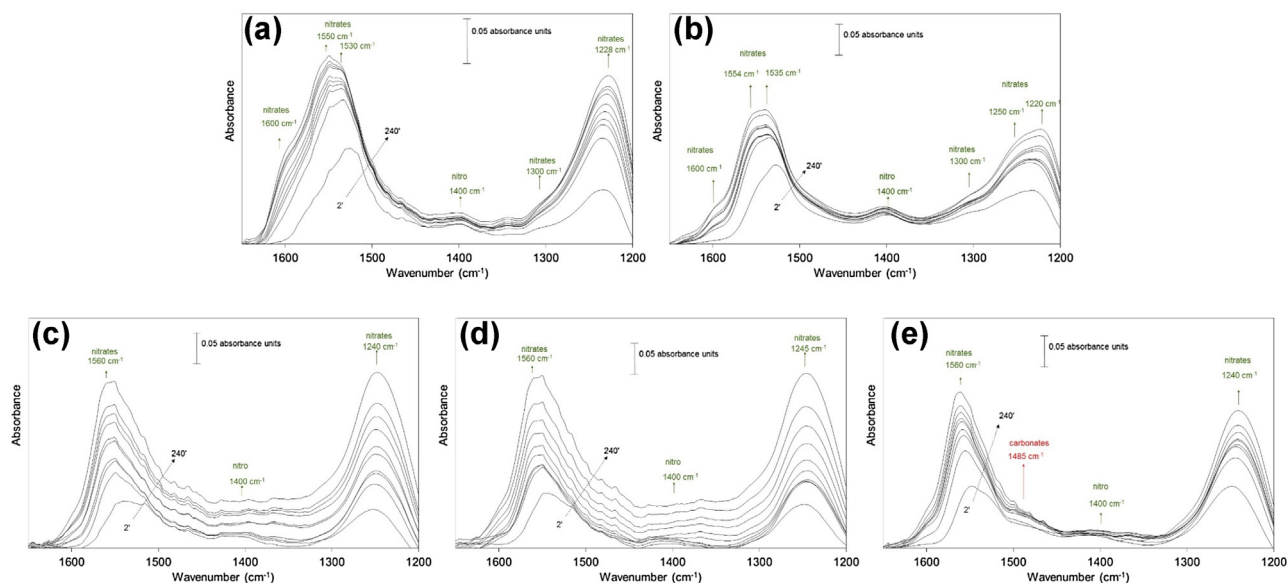

Fig. 5. DRIFT spectra monitored as a function of time during isothermal experiments performed at 400 °C with 1:20 loose contact soot-catalyst mixtures (without H$_2$ pulses). (a) CuO/Ce$_{0.8}$Zr$_{0.2}$O$_\delta$, (b) CuO/CeO$_2$, (c) CuO/Ce$_{0.8}$Nd$_{0.2}$O$_\delta$, (d) CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$ and (e) CuO/Ce$_{0.8}$La$_{0.2}$O$_\delta$.
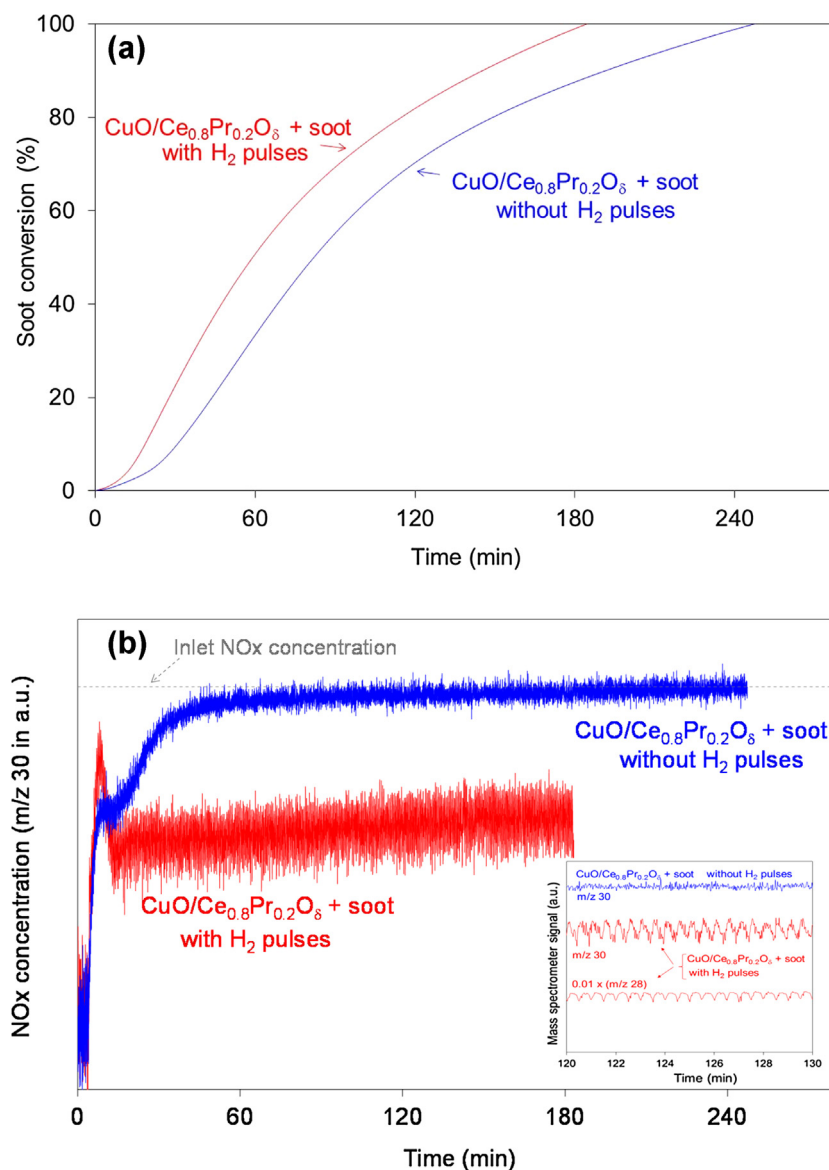
Fig. 6. Isothermal experiments performed at 400 °C with 1:20 loose contact soot-CuO/Ce$_{0.8}$Pr$_{0.2}$O$_{\delta}$ mixtures with and without H$_2$ pulses. (a) Soot conversion and (b) NOx concentration.

interpretations could contribute and may be related to each other. That is, the destabilization of the chemisorbed NOx species could be due to the chemisorption of CO$_2$ emitted upon soot combustion, but other destabilization mechanisms could be also feasible and, with the experimental evidence available, it is not possible to confirm which is the main contributing factor.

The DRIFT spectra recorded under operando conditions isothermally at 400 °C with soot-CuO/Ce$_{0.8}$M$_{0.2}$O$_{\delta}$ mixtures provide valuable information regarding chemisorption of NOx on the catalysts and about the influence of soot combustion in this process. These DRIFT spectra are shown in Fig. 5 for all catalysts.

The main bands that grow with time around 1550 and 1230 cm^{-1} can be assigned to nitrates [39], in agreement with the conclusions of the temperature programmed experiments. Nitrates of different configuration were formed on CuO/Ce$_{0.8}$Zr$_{0.2}$O$_{\delta}$ (Fig. 1a) and CuO/CeO$_2$ (Fig. 1b) catalysts, as deduced for instance, from the maxima at ∼1600, ∼1550 and ∼1530 cm^{-1} that would be consistent with the formation of bridging, bidentate and monodentate nitrates, respectively. On the contrary, the position of the nitrate

bands for catalysts with Nd, Pr or La are consistent with the formation bidentate nitrates. The formation of nitro groups is also inferred from the bands at 1400 cm^{-1} [39], and these species seem to remain stable during the whole experiment for CuO/Ce$_{0.8}$Zr$_{0.2}$O$_{\delta}$ and CuO/CeO$_2$ but not in the case of Nd, Pr or La.

In addition to nitrogen species, a shoulder is observed at 1485 cm^{-1} in the spectra (Fig. 5e) of the catalyst containing the most basic dopant (CuO/Ce$_{0.}$La$_{0.2}$O$_{\delta}$) that could be assigned to carbonates. This would support the hypothesis that the chemisorption of the CO$_2$ produced by soot combustion competes with the chemisorption of NOx and would explain why the CuO/Ce$_{0.}$La$_{0.2}$O$_{\delta}$ catalyst chemisorbs much more NOx in the absence than in the presence of soot (Fig. 4e and Table 1). This band at 1485 cm^{-1} due to carbonates was not so obvious in the spectra of the other catalysts, although a certain level of carbonation cannot be ruled out as discussed elsewhere [43]. The differences in terms of the 1485 cm^{-1} band intensity would be consistent with the fact that catalysts with basic dopants are more prone to suffer the negative effects of soot
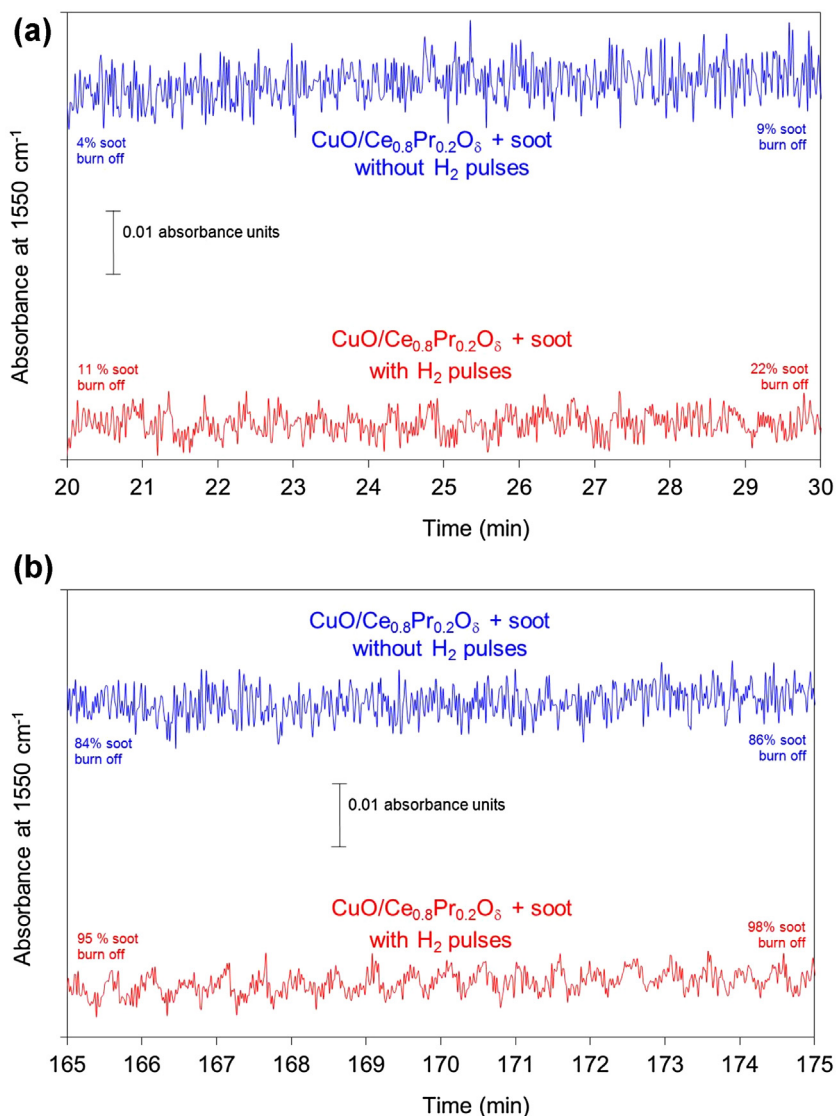
Fig. 7. Absorbance at 1550 cm^{-1} (nitrates) monitored by rapid-scan DRIFTS during isothermal experiments performed at 400 °C with 1:20 loose contact soot-CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$ mixtures with and without H$_2$ pulses. (a) minutes 20–30 (b) minutes 165–175.

on NOx chemisorption due to the CO$_2$ emitted as a soot combustion product.

3.3. Isothermal experiments at 400 °C with H$_2$ pulses

An isothermal soot combustion experiment was performed at 400 °C with CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$ and H$_2$ pulses, and the results are shown in Fig. 6 together with those of a similar experiment performed without H$_2$. CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$ was the most active catalyst for NOx chemisorption (Table 1) and soot combustion (Fig. 3) after CuO/CeO$_2$. However, it is very well known that neat ceria is prone to deactivate under real operating conditions due to sintering, and so doping with other cations is essential to attain suitable thermal stability [40]. For this reason, CuO/Ce$_{0.8}$Pr$_{0.2}$O$_\delta$ was selected for this NSR experiment.

Fig. 6a presents the soot conversion profiles with and without H$_2$ pulses and Fig. 6b the corresponding NOx concentrations (m/z 30 signals). These results demonstrate that soot (Fig. 6a) and NOx (Fig. 6b) can be simultaneously removed following the NSR approach (see curves obtained with H$_2$ pulses). As it is shown in the inset of Fig. 6b, the NOx profile obtained in the experiment with H$_2$ pulses follows the shape of the pulses because, once H$_2$

was introduced, most of the NOx stored on the catalyst was reduced yielding N$_2$ and a small fraction was released without undergoing reduction. The release of N$_2$ as NOx reduction product is deduced from the shape of the m/z 28 signal, which also follows the shape of the pulses. The high selectivity of the Copper/Ceria NSR catalysts towards N$_2$ formation was also observed in the previous articles of this series [22,23]. It is worth noting that the potential release of CO as soot combustion product could contribute to the m/z 28 signal, and this would affect the interpretation of the m/z 28 profile and the assignation to N$_2$. However, the formation of CO as soot combustion product is not expected. CO was not observed during the experiment performed without H$_2$ pulses and is neither expected to be released in the experiments with H$_2$.

NOx removal by the NSR method had a positive effect on the catalytic combustion of soot. Soot oxidation took place faster when H$_2$ was pulsed (compare curves in Fig. 6a), and two arguments can be postulated to explain this observation: (i) the destabilization of the stored nitrates upon H$_2$ pulses leads to the formation of high local concentrations of NO$_2$ that contribute to soot combustion because NO$_2$ is highly oxidizing and/or (ii) the oxidation of H$_2$ leads to the localised increase in temperature, which enhances soot combustion.

The nature of the species chemisorbed on the catalyst during these isothermal soot combustion experiments was monitored by rapid-scan DRIFTS, and only nitrates were detected. The band at $1550\,cm^{-1}$ due to nitrates was selected to monitor changes in their population during the isothermal experiments, and the absorbance at this wavenumber as a function of time is plotted in Fig. 7. The nitrate band intensity monitored during the experiment performed without H_2 pulses shows fluctuations only arising from signal noise. In contrast, the absorbance at $1550\,cm^{-1}$ monitored during H_2 pulses followed the shape of the pulses, in accordance with the results obtained in NSR experiments performed with the $CuO/Ce_{0.8}M_{0.2}O_\delta$ catalysts (without soot) discussed in a previous article [23]. This shape is produced because the H_2 pulse partially regenerates the catalyst, which is again saturated with NOx between consecutive pulses. Note that the peaks of the profile of absorbance at $1550\,cm^{-1}$ in the experiments with H_2 pulses were much better defined when soot was almost consumed (Fig. 7b; 95–98% soot burn off) than when soot was still available in quantity and thus undergoing significant reaction (Fig. 1a; 11–22% burn off). This could indicate that the depletion of surface nitrates during the combustion of soot under NSR conditions not only occurs due to the H_2 pulses but also due to reaction with soot.

In conclusion, it is demonstrated that the simultaneous removal of NOx and soot can be carried out under NSR conditions at $400\,°C$ with a $5\%Cu/Ce_{0.8}Pr_{0.2}O_\delta$ catalyst, and the NSR process has a positive effect on soot combustion.

4. Conclusions

Copper catalysts with $Ce_{0.8}M_{0.2}O_\delta$ supports (M = Zr, La, Ce, Pr or Nd) were studied for the simultaneous combustion of soot and removal of NOx by the NSR method, and the following conclusions can be drawn:

- The simultaneous chemisorption of NOx and combustion of soot can be carried out above $375\,°C$. Above this temperature the main NOx species stored on the catalysts were nitrates in different configurations, providing evidence that the oxidation capacity of the catalysts was sufficiently high to oxidise N (II) (in NO) to N (V) (nitrates).
- The presence of soot affects the chemisorption of NOx on the catalysts, and the nature of the M dopant plays an important role in the chemisorption of NOx and in the catalysed soot-NOx reaction. As a general trend, the presence of soot is negative for NOx removal by catalysts with very basic supports while is null or positive if the support is not very basic.
- The combustion of soot has a detrimental effect on NOx chemisorption on the catalyst with the most basic dopant ($CuO/Ce_{0.8}La_{0.2}O_\delta$), because the chemisorption of CO_2 emitted as a soot combustion product competes with NOx for the adsorption sites.
- In contrast, soot combustion does not affect NOx chemisorption on the catalyst with the most acidic dopant ($CuO/Ce_{0.8}Zr_{0.2}O_\delta$), and the removal of NOx increases in this case because the reduction NOx by soot also removes NOx.
- The simultaneous removal of NOx and soot can be carried out under NSR conditions at $400\,°C$ with the $5\%Cu/Ce_{0.8}Pr_{0.2}O_\delta$ catalyst and with H_2 micropulses, and the NSR process improves the catalytic combustion of soot.

Acknowledgements

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